



Technology Transfer in Energy Sector



PHOTOCATALYSIS OF AMMONIA FOR HYDROGEN PRODUCTION

2025

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- This work aims to present an overview of recent advancements in research and development (R&D) focused on cost-effective and environmentally sustainable methods for hydrogen production.
- Ammonia is widely recognized for its significant potential as a versatile material for hydrogen transport and production. In addition, it is a fundamental and highly valuable chemical product in its own right.
- The primary focus of this document is on photocatalytic methods, with a particular emphasis on those developed at Rice University in recent years.
- The objectives of this work are as follows:
 - ✓ To build upon the fundamental principles of chemical physics by elucidating the basic mechanisms underlying photocatalytic processes.
 - ✓ To provide readers with comprehensive knowledge, enabling them to understand and engage with the relevant technical literature.

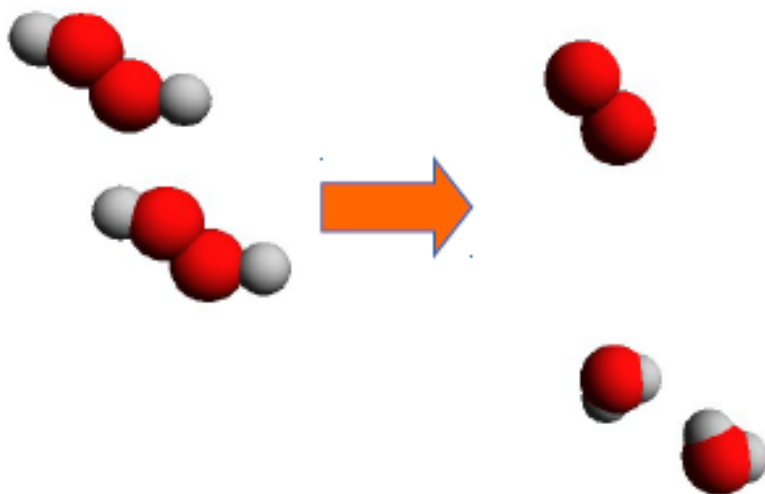


Image generated with Avogadro v. 1.2.0

Time to complete: several weeks

In the presence of MnO_2
reaction completes in
minutes

Decomposition of H_2O_2 (Hydrogen Peroxide)

Chemical Reaction Rate

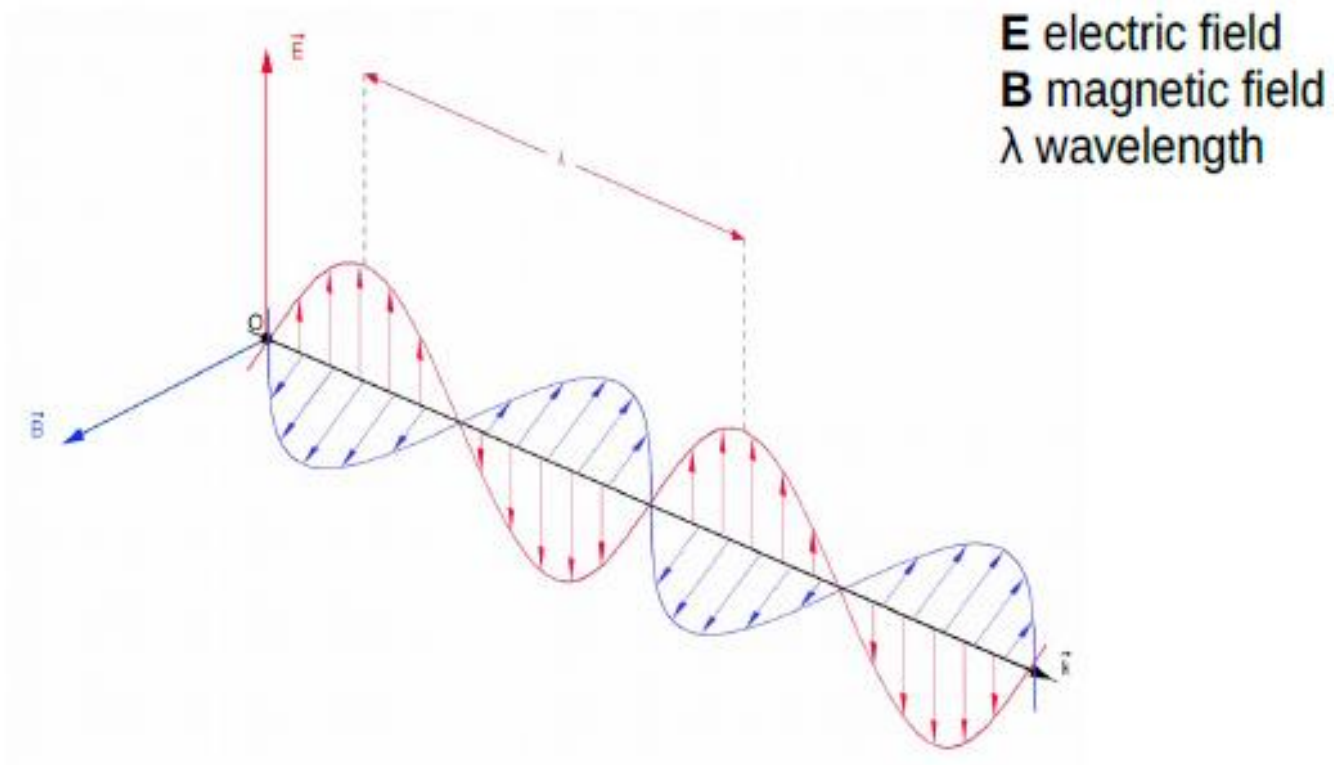
- In simple terms, the chemical reaction rate describes how quickly a chemical reaction occurs.
- More technically, it is defined as the number of moles of a specific chemical substance (typically the reaction product) formed per unit time.

Catalysis

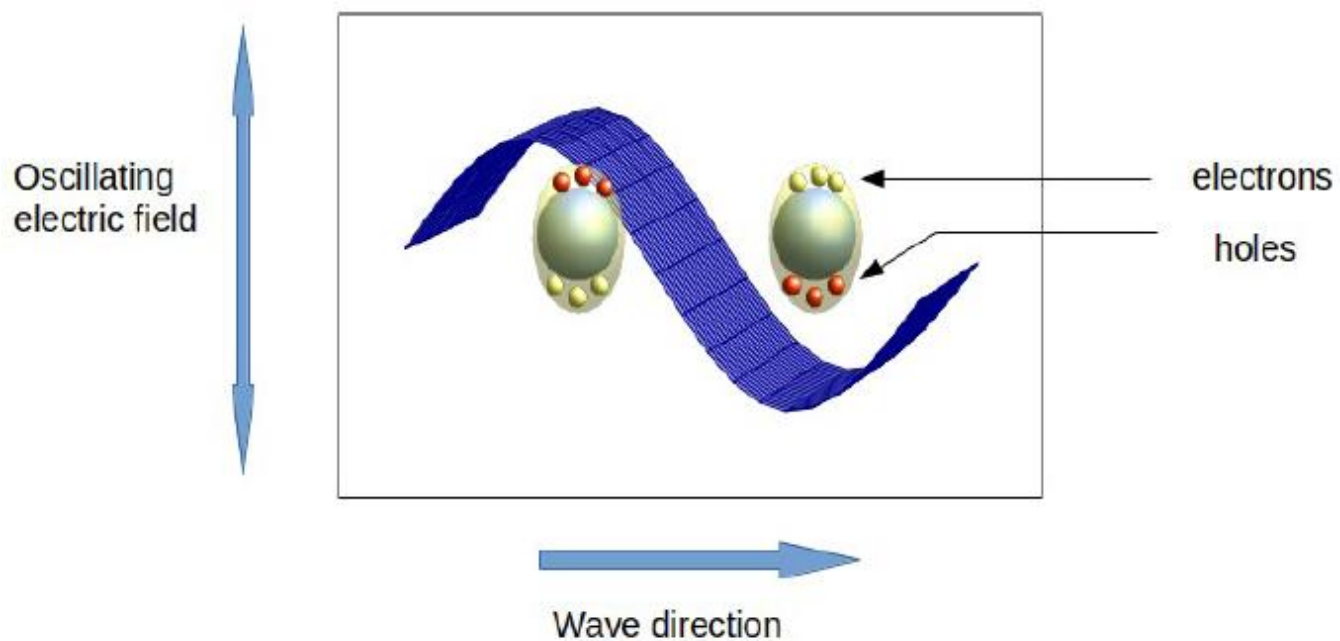
- Catalysis is the process by which the rate of a chemical reaction is significantly increased.
- This enhancement occurs due to the presence of a catalyst.
- ***Catalyst:***
 - ✓ A catalyst is a chemical substance that participates in a chemical reaction and increases its rate without undergoing any permanent chemical change itself.
 - ✓ Enzymes, found in living organisms, serve as prominent examples of catalysts

- Light is a form of electromagnetic radiation, characterized by oscillating electric and magnetic fields that are perpendicular to each other and to the direction of wave propagation.
- In photocatalysis, the oscillating electric field of light plays a pivotal role in driving the process. Notably, extraordinary phenomena arise when an electromagnetic wave interacts with a small particle. If the particle's size is smaller than the wavelength of the incident light, remarkable effects can occur, profoundly influencing the behavior and outcomes of the system.

THE ELECTROMAGNETIC WAVE



THE ELECTROMAGNETIC WAVE



PLASMA AND PLASMON

- In physics, plasma refers to a gas of charged particles, typically consisting of negatively charged electrons and positively charged atomic ions.
- Within materials, electrons are distributed across distinct energy levels based on their energy content, which arises from the electrostatic interactions between electrons and atomic nuclei. Electrons in the high-energy conduction band behave as a plasma. This plasma oscillates collectively in response to an external electric field.
- These oscillations give rise to a phenomenon known as a plasmon, which can be described as an elementary quantum particle. The practical significance of this behaviour lies in its potential to serve as an energy source for catalytic processes.

PLASMA AND PLASMON

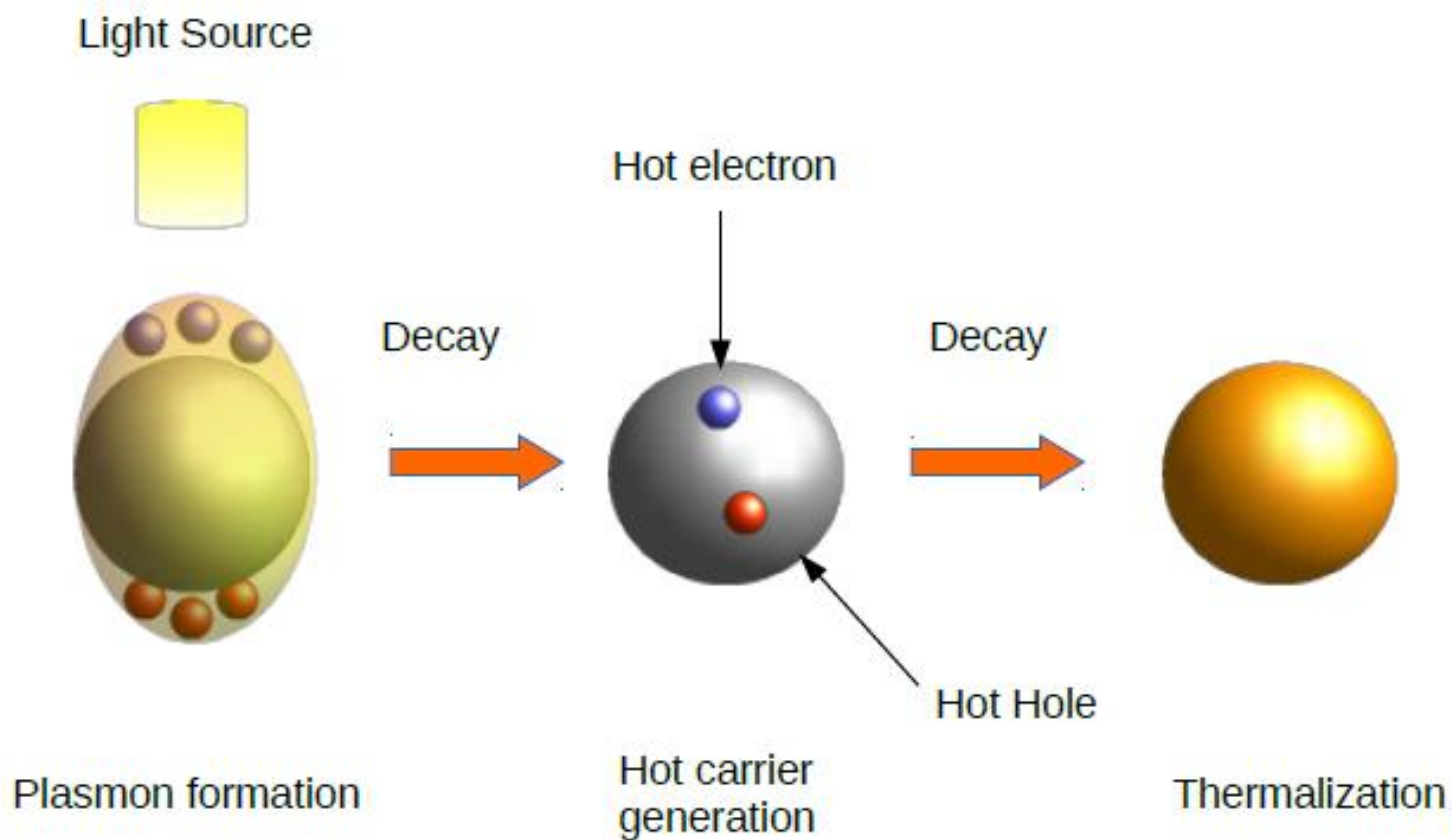
- *Localized Surface Plasmon Resonance (LSPR)* occurs when an oscillating electric field induces the formation of plasmons within a nanoparticle. These plasmons are confined to the surface of the nanoparticle. At specific frequencies of the oscillating field, corresponding to particular wavelengths of incident light, a resonance phenomenon takes place. This resonance condition leads to a significant increase in the absorption of light energy, resulting in a sharp peak in the extinction spectrum.
- *LSPR: Localized Surface Plasmon Resonance* - An oscillating electric field induces the formation of plasmons. In nanoparticles, these plasmons are confined to the particle's surface. When the frequency of the oscillating electric field matches specific wavelengths of the incident light, a resonance phenomenon occurs. At resonance, the energy captured from light (extinction) increases sharply, reaching a pronounced peak.

Plasmon Life Cycle

This simplified description outlines the key stages of a plasmon's lifecycle.

- ***Excitation:*** Upon illumination with a light source (e.g., an LED), collective oscillations of electrons within the metal nanoparticle are induced, forming a plasmon.
- ***Damping:*** The excited plasmon decays, releasing its energy.
- ***Hot Carrier Generation:*** A portion of the plasmon energy is transferred to electrons, elevating them to higher energy states. These high-energy electrons (hot carriers) are accompanied by the formation of holes (positive charges). These energetic charge carriers can participate in various chemical reactions.
- ***Thermalization:*** The remaining energy of the hot carriers and holes is transferred to the surrounding medium (e.g., the nanoparticle itself or the surrounding environment), resulting in an increase in temperature.
- ***Catalytic Activity:*** Even after thermalization, the nanoparticle may still exhibit catalytic activity, albeit through conventional thermally activated processes.

PLASMA AND PLASMON

Plasmon Life Cycle

SABATIER'S PLOT

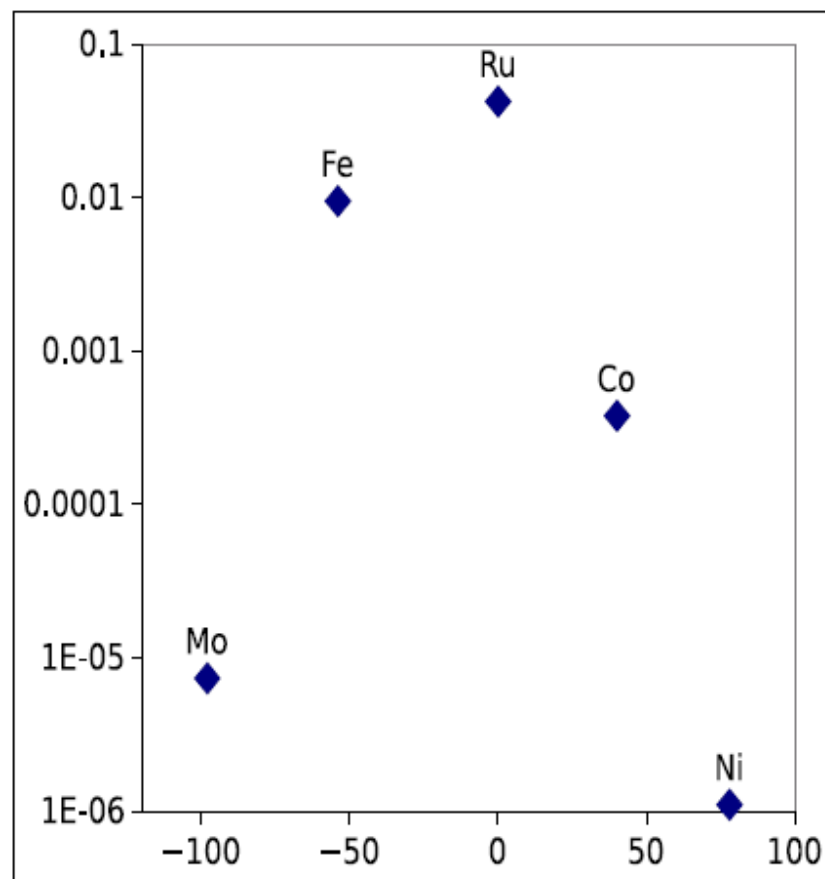
- This graph is utilized by specialists in catalyst design, particularly for reactions involving ammonia (NH_3) dissociation.
- For the chemical reaction to proceed, NH_3 must adsorb onto the catalyst surface, forming a temporary chemical bond. Subsequently, the actual reaction occurs, converting NH_3 into H_2 and N_2 , which then desorb from the surface.
- The reaction velocity is critically dependent on the delicate balance between the strength of the N-metal chemical bond and the rates of adsorption and desorption processes. Sabatier's plot visually illustrates this crucial effect.

SABATIER'S PLOT

- The abscissa of the plot represents the difference in bond energy between N_2 and a given metal catalyst, using the bond energy with Ruthenium (Ru) as the zero point. The ordinate displays the Turn Over Frequency (TOF), which quantifies the number of reactant molecules converted per active site per unit time. A higher TOF signifies a more efficient catalyst.
- The plot reveals an optimal range of metal catalysts for this reaction, with Iron (Fe) and Ruthenium (Ru) exhibiting peak performance.
- It's noteworthy that TOF values in industrial systems typically range from 100 to 0.01, whereas enzymes can exhibit remarkably high TOF values, reaching up to 10^7

SABATIER'S PLOT

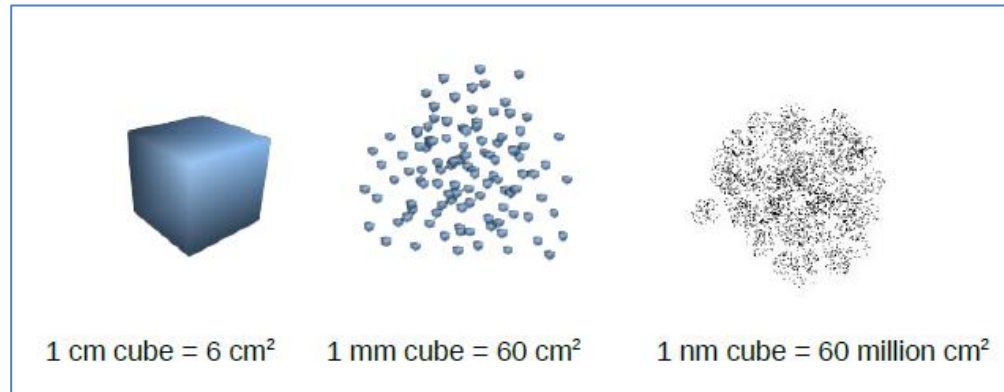
Turn-Over
Frequency
(TOF)



N-metal – N-Ru Relative Bond Strength

SABATIER'S PLOT

Role of surface area

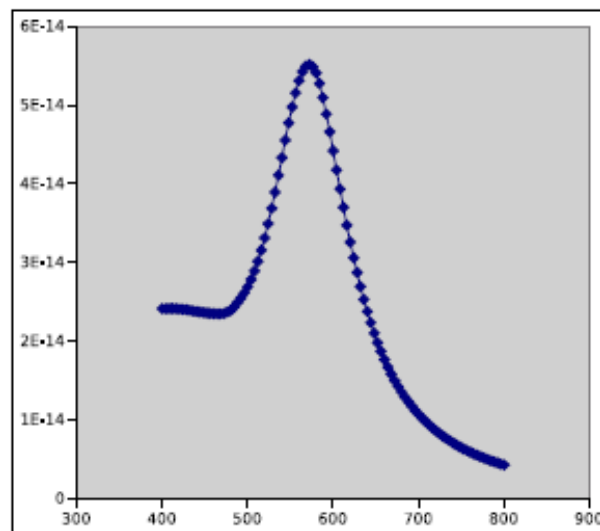


Surface Area increases with decreasing particle size at constant mass

- Illustrating the dramatic impact of size reduction on surface area: a decrease in particle size by seven orders of magnitude (from centimeters to nanometers), while maintaining the same mass, results in a corresponding increase in surface area. This significantly enhances several key properties.
- Firstly, a high surface area directly translates to a substantial increase in the material's adsorption capacity. Secondly, when particle dimensions are smaller than the wavelength of visible light, intriguing phenomena arise. Notably, charge separation occurs within the particles, leading to the formation of plasmons.

SABATIER'S PLOT

Light Extinction
(absorption cross
sectional area in m^2)



Particle diameter 50 nm

wavelength

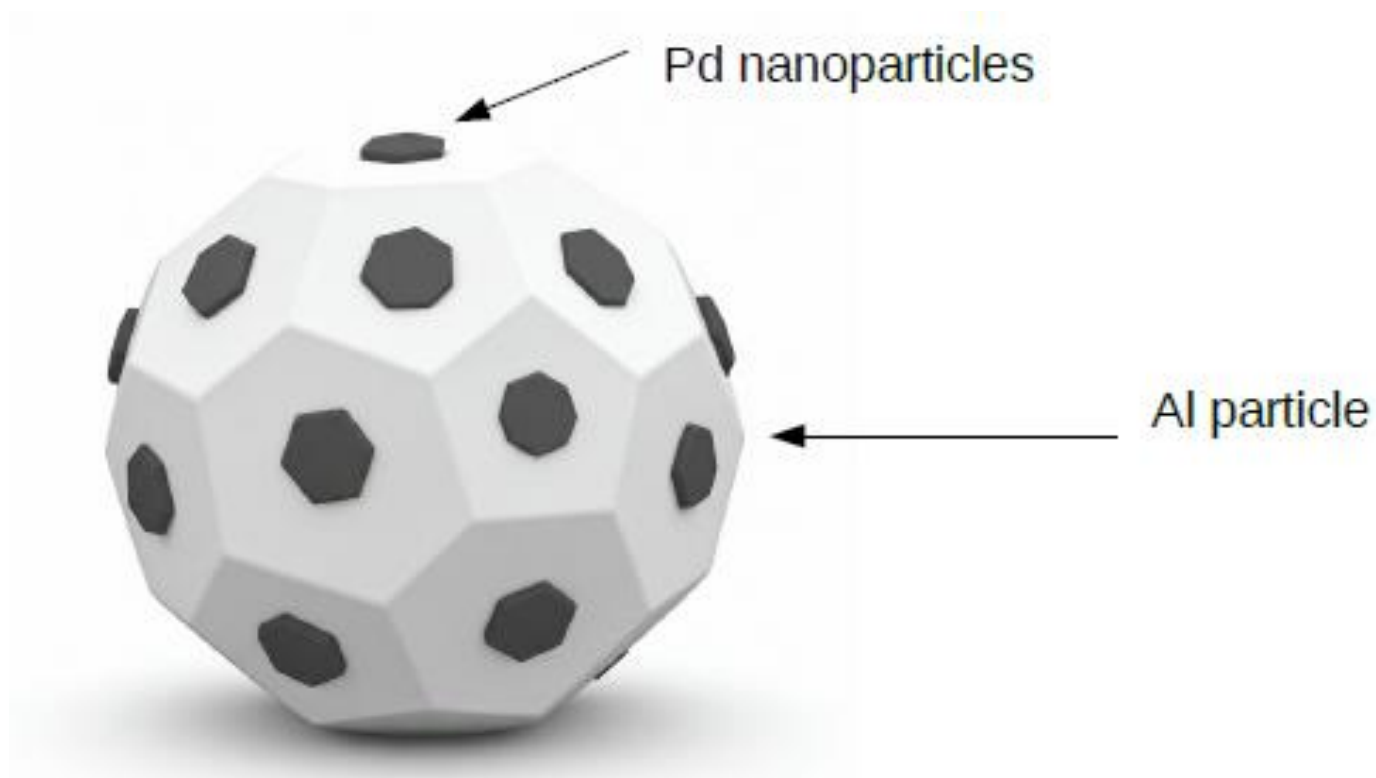
Localized Surface Plasmon Resonance in a Gold Nanoparticle

LIGHT EXTINCTION AND ABSORPTION CROSS SECTION

- In this context, light extinction is quantified by the absorption cross section, which represents the probability of light being captured by a nanoparticle. A larger cross-sectional area corresponds to greater light absorption, resulting in more energy being made available for photochemical reactions.
- The example illustrates the effect of resonance: for a gold nanoparticle with a diameter of 50 nm, the absorption peaks at a wavelength of 564 nm, corresponding to green yellow light. The resonant wavelength is influenced by the material, size, and shape of the nanoparticle.
- The calculations were performed using the Mie calculator provided by NanoComposix.

LIGHT EXTINCTION AND ABSORPTION CROSS SECTION

Al-Pd Antenna Reactor System



LIGHT EXTINCTION AND ABSORPTION CROSS SECTION

Pictorial Representation of an Al-Pd Antenna Reactor System

- This system features a relatively large aluminum (Al) particle (approximately 110 nm in diameter) that serves as an antenna. Several palladium (Pd) nanoparticles (approximately 10 nm in diameter) are grown on the surface of the Al particle.
- The Al crystal acts as an antenna, efficiently capturing incident light and generating surface plasmons. At the Al-Pd interface, where a thin layer of aluminum oxide is present, near-field enhancement effects significantly amplify the energy transfer to the Pd nanoparticles. The presence of the dielectric oxide layer locally intensifies the electric field generated by the plasmons.

LIGHT EXTINCTION AND ABSORPTION CROSS SECTION

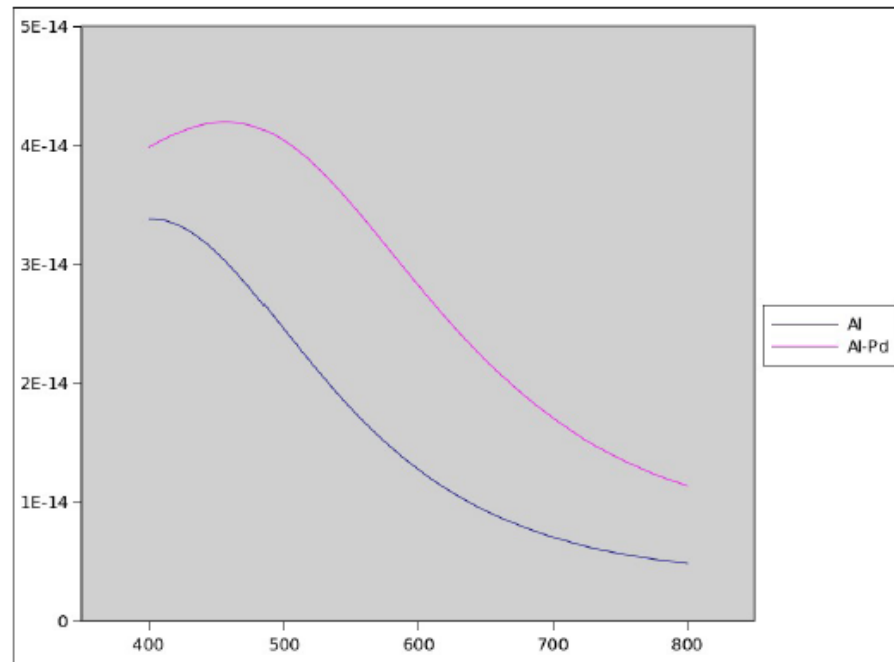
Optical Efficiency of Nanoparticles

- The plot in the figure compares the extinction spectra of a pure aluminum (Al) nanoparticle with that of a mixed aluminum-palladium (Al-Pd) nanoparticle.
- The spectra were obtained through simulations using the Nanocomposix Mie Theory Calculator, with aluminum selected as the core material and palladium as the shell material.
- Although the actual extinction spectrum of a "decorated" particle may differ due to various factors, the simulation effectively demonstrates how material mixing can enhance optical efficiency.

LIGHT EXTINCTION AND ABSORPTION CROSS SECTION

Optical Efficiency of Nanoparticles

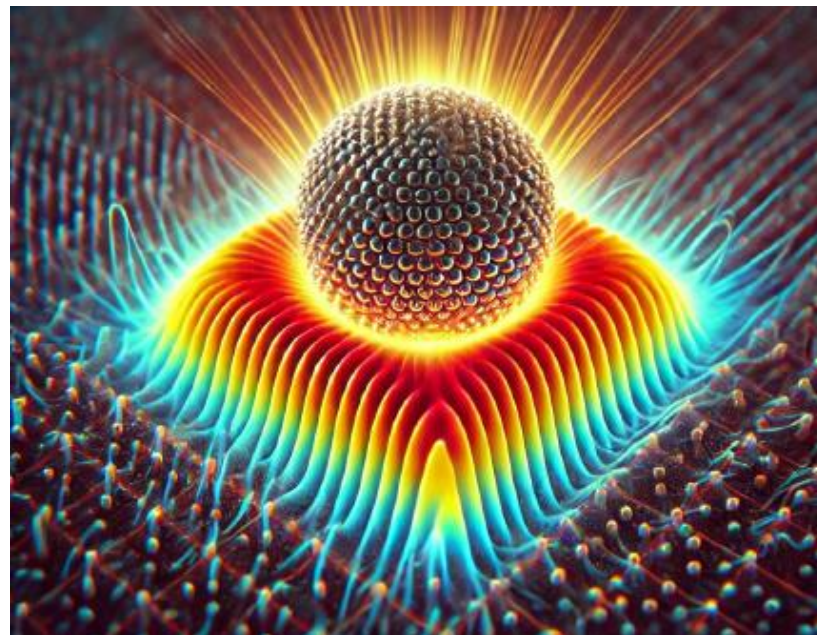
Extinction
Cross
Section
 m^2



Wavelength (nm)

NEAR-FIELD ENHANCEMENT EFFECT: ARTIST'S VIEW

- This image illustrates the near field enhancement effect at the interface between a substrate particle and a nanoparticle attached to it.



- The colors in the image correspond to the intensity of the electromagnetic field generated by plasmons, with the highest field intensity concentrated around the nanoparticle. This intense electromagnetic field significantly enhances the nanoparticle's catalytic properties.

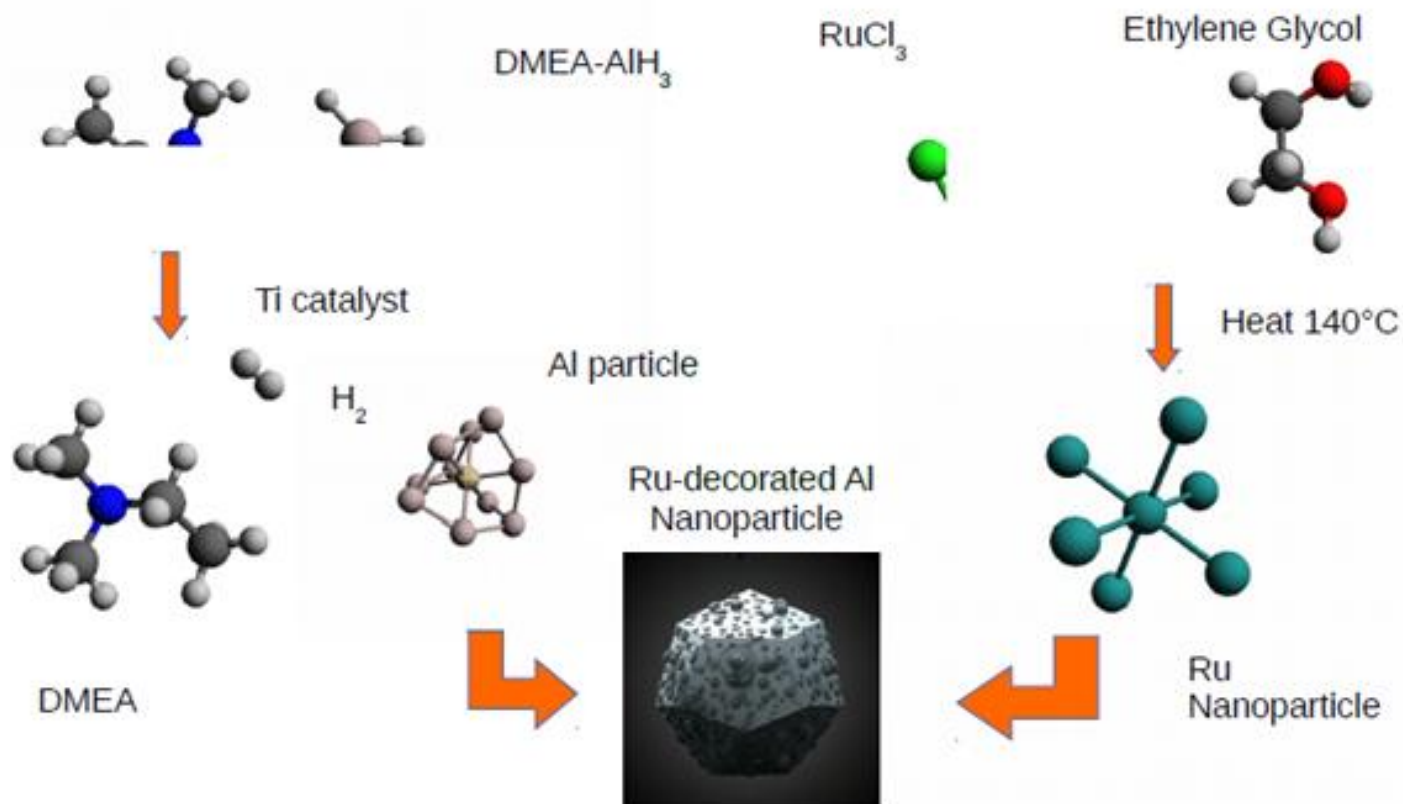
Al-Pd HETERODIMER

- This pictorial view represents a microscopic assembly consisting of an aluminum (Al) and a palladium (Pd) disk, forming an Al-Pd heterodimer. An experimental setup comprising a large ensemble of these nanoscale disks was employed to demonstrate the near-field enhancement effect on a model reaction: the conversion of molecular hydrogen (H_2) to hydrogen-deuterium (HD).
- Rigorous laboratory experiments revealed a significant enhancement in the reaction rate upon light stimulation. Specifically, the observed reaction rate under light irradiation was five times higher compared to the rate observed in the absence of light (i.e., under purely thermally activated conditions).



Al-Pd Heterodimer

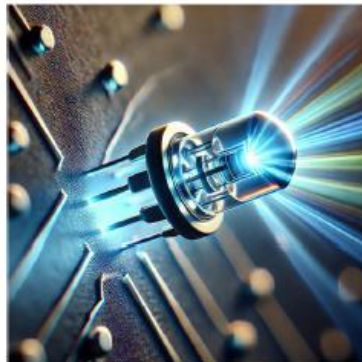
DECORATED NANOPARTICLE SYNTHESIS



DECORATED NANOPARTICLE SYNTHESIS

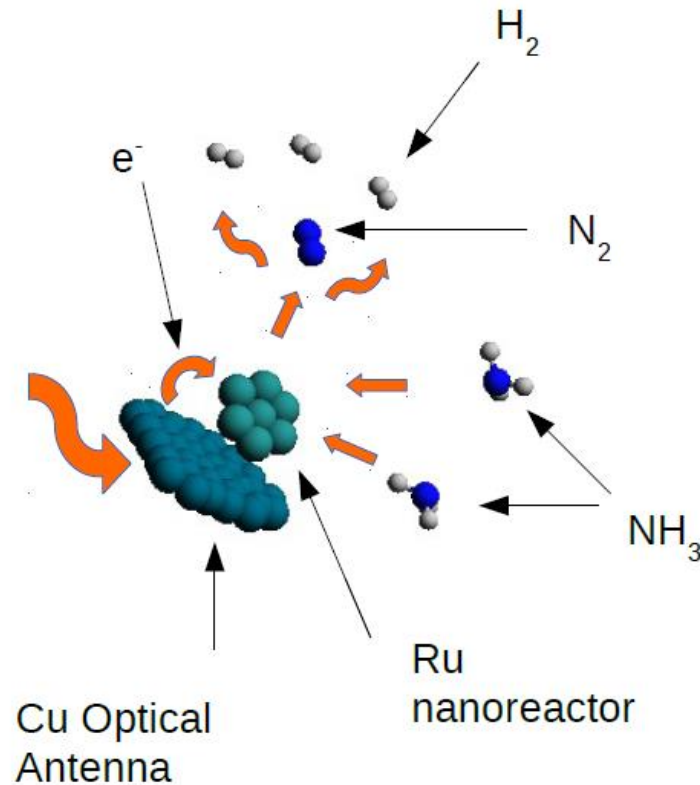
- Particles for plasmonic photocatalysis are synthesized via a two-step process.
- Firstly, the aluminum (Al) support particle is synthesized according to the reaction depicted in the image. Subsequently, metal nanoparticles are grown onto the surface of the Al particle. This growth step involves heating a metal precursor salt in the presence of ethylene glycol, which serves as both a solvent and a reducing agent. The synthesis of Ru nanoparticles on the Al support is presented as an illustrative example.
- This two-step approach enables precise control over both the dimensions and the shape of the resulting decorated particle.

ANTENNA-REACTOR EXAMPLE: AMMONIA DECOMPOSITION ON Pd-Ru



LED Light
Pulses

Image generated with Avogadro v.
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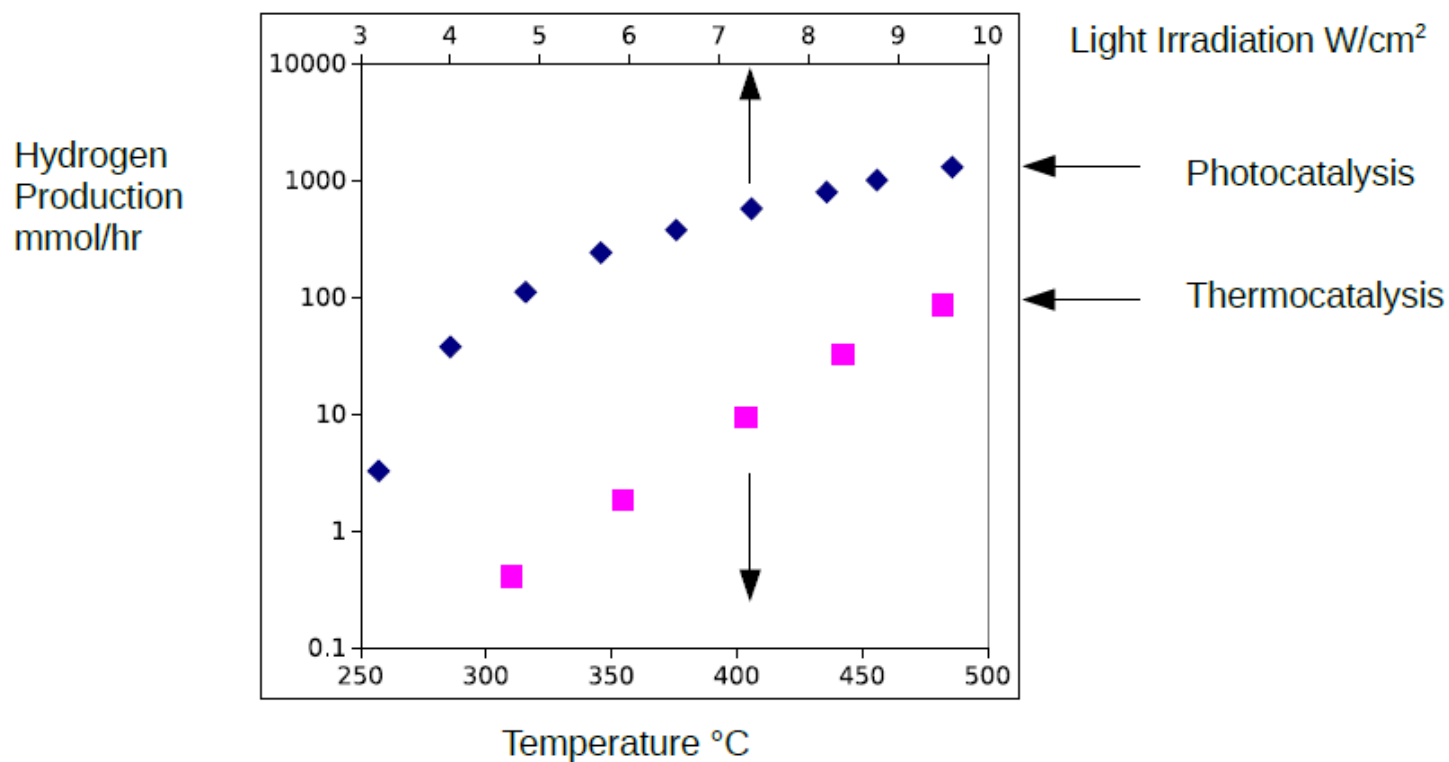
- The image above depicts an experimental setup for ammonia decomposition. This system utilizes a combination of a copper (Cu) particle, acting as an antenna to capture light emitted by an LED source, and a palladium (Pd) nanoparticle, serving as the active catalyst.

ANTENNA-REACTOR EXAMPLE: AMMONIA DECOMPOSITION ON Pd-Ru

- The rationale for employing two distinct materials lies in the inherent trade-off between optical and catalytic properties. Materials with excellent optical properties for light absorption often exhibit suboptimal catalytic activity, and vice versa.
- However, by combining these functionalities through the Cu-Pd heterostructure, the system demonstrates promising results in terms of energy efficiency and favorable chemical kinetics.

ANTENNA-REACTOR EXAMPLE: AMMONIA DECOMPOSITION ON Pd-Ru

Photochemical vs. Thermochemical Ammonia Decomposition



Comparison between Photocatalytic and Thermocatalytic Ammonia Decomposition

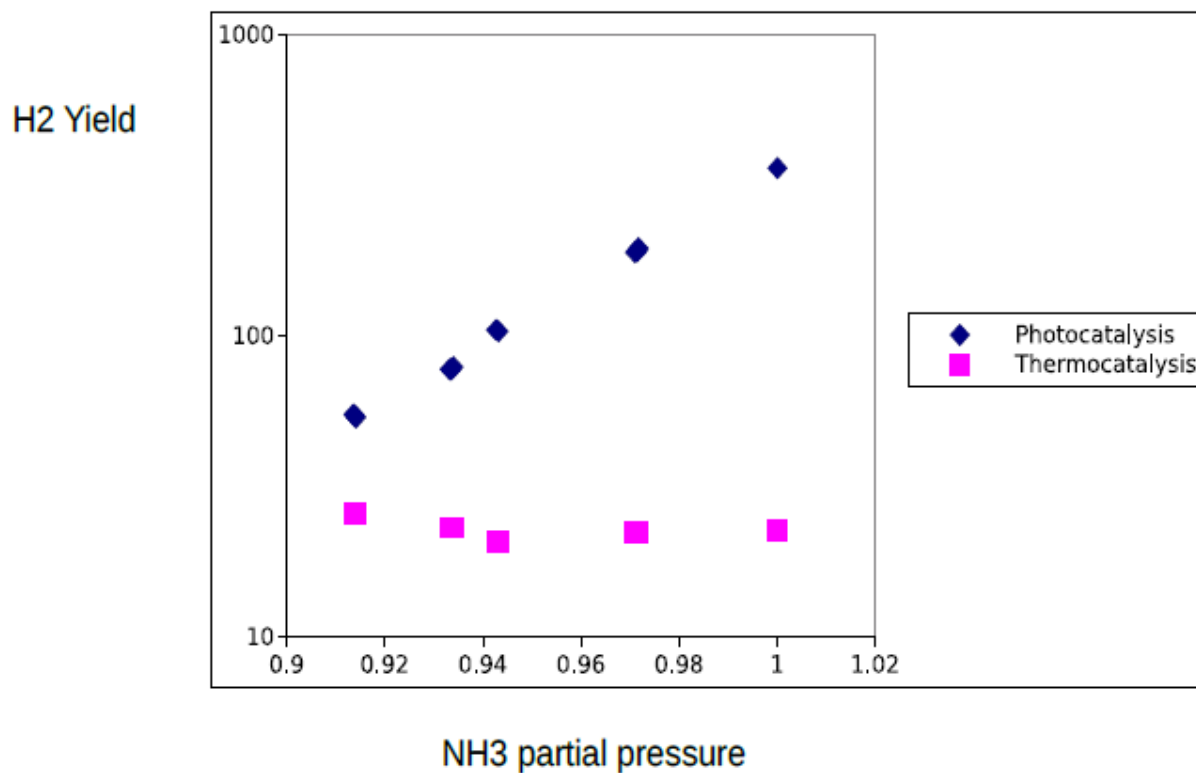
ANTENNA-REACTOR EXAMPLE: AMMONIA DECOMPOSITION ON Pd-Ru

Photochemical vs. Thermochemical Ammonia Decomposition

- The plot compares hydrogen (H_2) production rates as a function of temperature for thermocatalytic reactions (lower x-axis) and illumination intensity for photocatalytic reactions (upper x-axis).
- In the thermocatalytic regime, the highest measured H_2 production rates as a function of temperature for production rate is achieved at 480°C . In contrast, photocatalysis achieves the same H_2 production rates as a function of temperature for production rate at room temperature under moderate illumination conditions (approximately 5 W/cm^2).
- This comparison underscores the significant advantage of photocatalysis, offering substantially reduced energy consumption and, consequently, lower costs for H_2 production rates as a function of temperature for production.

ANTENNA-REACTOR EXAMPLE: AMMONIA DECOMPOSITION ON Pd-Ru

Photochemical vs. Thermochemical Ammonia Decomposition



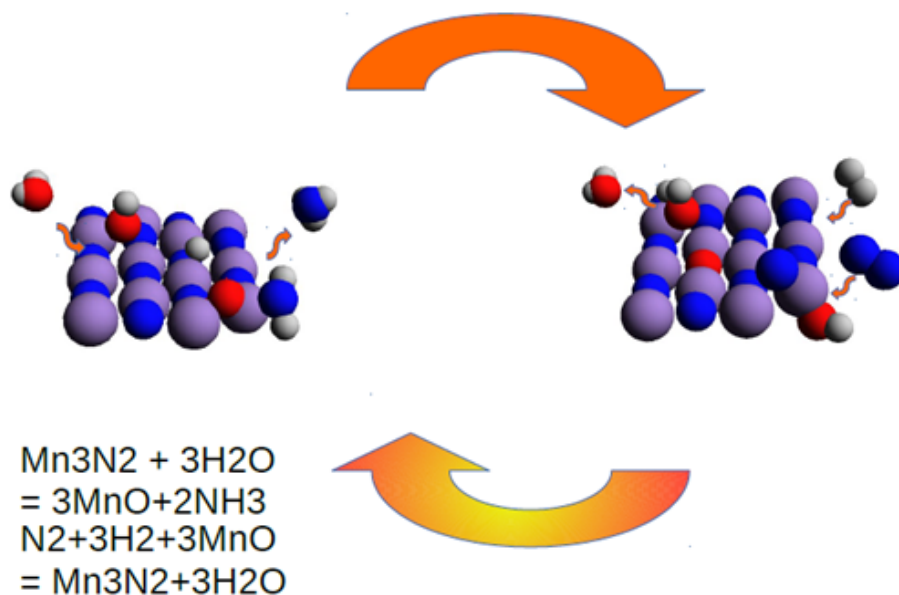
Plot of H₂ Yield vs. NH₃ Partial Pressure in Photocatalytic and Thermochemical Reaction Regimes

LIGHT-DRIVEN CHEMICAL LOOPING FOR AMMONIA PRODUCTION

- The term “chemical looping” was born in the context of fuel-based energy production.
- Presently, significant attention is paid to the opportunity to use chemical looping to produce hydrogen and other chemicals as well.
- Chemical looping commonly refers to cyclic processes that utilize a solid material as an oxygen carrier to facilitate fuel conversion. This solid material typically comprises metal oxide particles and acts as a circulating medium for oxygen.
- To complete the chemical loop, the oxygen-depleted solid carrier must undergo reoxidation before starting a new cycle. Traditionally, this re-oxidation step is carried out using air. However, when the process is tailored for chemical production, oxygen carrier materials are regenerated using CO_2 or H_2O instead of air, resulting in the respective production of CO_2 and H_2 .

LIGHT-DRIVEN CHEMICAL LOOPING FOR AMMONIA PRODUCTION

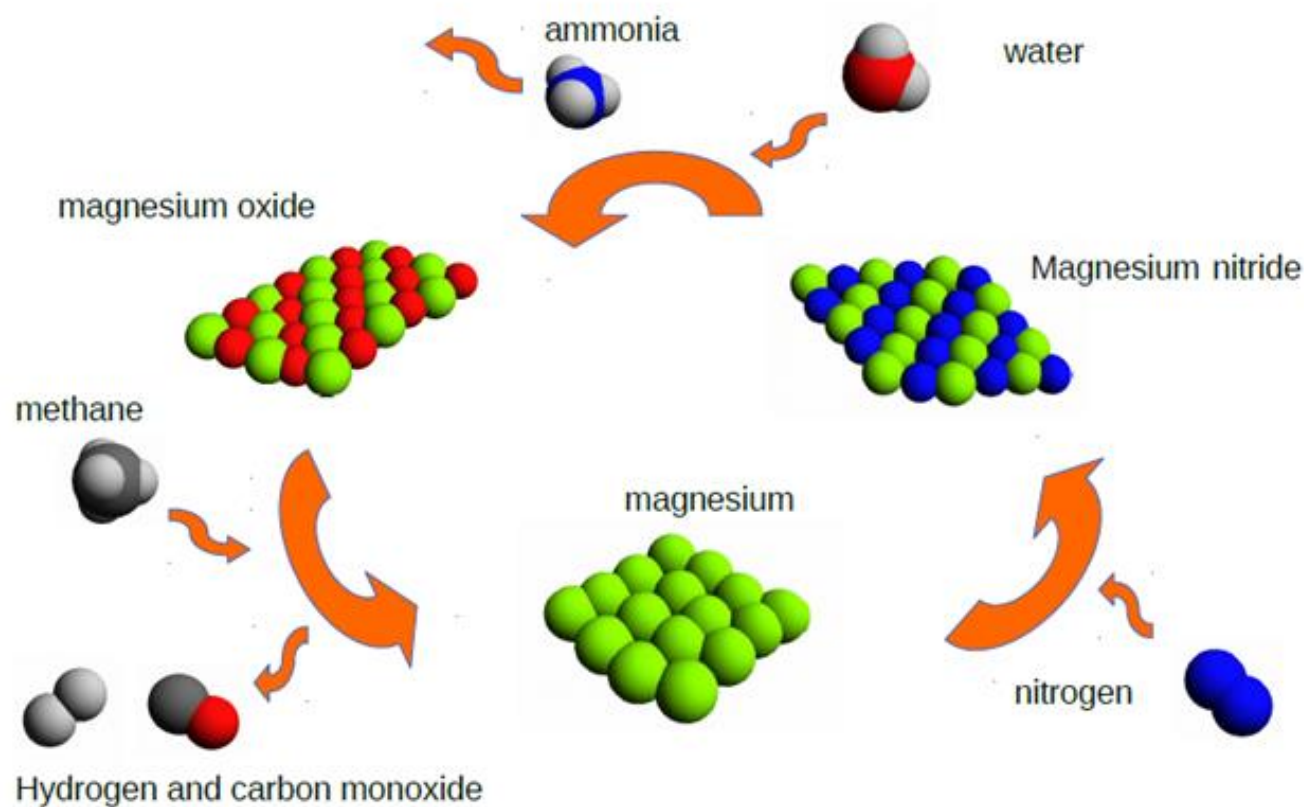
- The illustration depicts an example of ammonia synthesis through a chemical looping process.
- In this cycle, manganese nitride (MnN) reacts with water to produce ammonia, partially converting MnN into manganese oxide (MnO).



LIGHT-DRIVEN CHEMICAL LOOPING FOR AMMONIA PRODUCTION

- Subsequently, using concentrated solar radiation to increase the temperature, MnO is regenerated back into MnN using nitrogen and hydrogen.
- Similar chemical cycles can be designed with nanoparticle-based antenna-reactor systems to enhance efficiency and enable sustainable ammonia production.

LIGHT-DRIVEN CHEMICAL LOOPING FOR AMMONIA PRODUCTION



LIGHT-DRIVEN CHEMICAL LOOPING FOR AMMONIA PRODUCTION

- The cyclic reaction scheme illustrated in the figure depicts a chemical process occurring within an antenna reactor system. In this system, Titanium Nitride (TiN) functions as the antenna, while Magnesium Oxide (MgO) serves as the reactor.
- The cycle initiates with the reduction of MgO to magnesium metal (Mg) by methane. This reduction process is facilitated by the presence of TiN, which absorbs light and subsequently transfers hot electrons to MgO. Concurrently, carbon monoxide and hydrogen are liberated. In the second step, nitrogen reacts with Mg to form magnesium nitride. Subsequently, water reacts with magnesium nitride to produce ammonia and regenerate magnesium oxide.
- It is important to note that all these reactions occur via a photothermal mechanism. The localized absorption of light at the TiN antenna leads to a significant increase in temperature at the reactor surface, reaching temperatures as high as 500°C. This elevated temperature facilitates the necessary chemical transformations within the system.

FUTURE PROSPECTS OF PHOTOCATALYSIS

- The potential applications of photocatalytic methods extend far beyond hydrogen production. A wide range of industrially significant reactions could benefit from highyield, selective photochemical methods.
- *Dry Reforming:* Currently, dry reforming is an energy-intensive process with a substantial carbon footprint. Photocatalysis offers the potential to significantly improve its efficiency while reducing its environmental impact.
- *Methanol Synthesis:* Methanol production is another promising area, as methanol serves as a fundamental feedstock for numerous industrial applications.

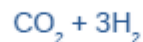
FUTURE PROSPECTS OF PHOTOCATALYSIS

- *Fischer-Tropsch Synthesis*: Photocatalysis could enhance this widely used process in two key ways—by reducing energy consumption and improving selectivity, addressing a well-known challenge associated with this method.
- *Claus Process*: Widely employed for desulfurization of hydrocarbon streams, the Claus process faces issues related to catalyst poisoning. Photocatalysis, supported by Al-NC particles, could mitigate this problem. The non-thermal desorption effect in such nanoparticles would help prevent the formation and irreversible adsorption of poisoning substances, ensuring more robust catalyst performance.

Dry Reforming (Syngas)



Methanol Synthesis



Selective Fischer Tropsch



Claus Process (Desulfurization)





Technology Transfer in Energy Sector

Elaborated by Carlo Carniani – Senior Petroleum Engineer